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THE INTERFACE STRUCTURE IN GRAPHITE/ALUMINUM COMPOSITES, (U)  
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## THE INTERFACE STRUCTURE IN GRAPHITE/ ALUMINUM COMPOSITES

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### Abstract

Transmission electron diffraction and Auger electron spectroscopy studies of the interfaces of selected graphite/aluminum composite systems revealed that generally titanium diboride, ( $TiB_2$ ), and aluminum oxide, ( $Al_2O_3$ ), were present as the interfacial phases. The grain size and the crystallographic structure of these interfacial phases were studied and are discussed in terms of the transverse fracture behavior of the graphite/aluminum composites.

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(TEM). The corresponding interface chemistry on some specimens was studied using a Scanning Auger Microscope (SAM). Various composite materials with different transverse strengths were employed in order to correlate the structure of interface phase with mechanical properties.

Titanium diboride ( $TiB_2$ ) was found in the interface layer for every material processed by the standard pretreatment coating.  $\gamma$ -Aluminum oxide ( $\gamma-Al_2O_3$ ) phase was also observed in most materials studied here as were other oxides and carbides.

#### Experimental

The graphite/aluminum composite materials examined in this study are listed in Table 1 along with fiber type, transverse strength and the interface phases observed in TEM. Except for G3842 which is plate consolidated from T133 wire, the materials are all unconsolidated wires. The matrix material is 6061 Al. The single fiber wire in Table 1 is a single graphite fiber "prepreg" with no pretreatment coating on the interface. This composite wire is produced by the ion vapor deposition of an aluminum 4% Mg alloy on the fiber. Basically, two fiber types were examined in this study, each representing currently available commercial forms. One is a low modulus type II PAN fiber with the oriented graphite basal planes tending to be parallel to the fiber

surface just below it. The other is a high modulus pitch type fiber with basal planes roughly perpendicular to the fiber surface. All fibers have circular cross sections. See Figure 1 for the relative basal plane orientation.

To make the fiber-matrix interface accessible to observation, a selective etching method was used. The materials were dipped or swabbed in one of three different etchants: a concentrated HCl solution, an HCl solution diluted by 60-70% volume percent methanol, and a 7N KOH solution. The samples were then thoroughly rinsed with acetone, methanol or ultrasonically cleaned in methanol. Thus, the sample fibers were free of the aluminum matrix material and only some interface pieces still attached to the fiber surface were left. Searching along the fiber surfaces in the transmission electron microscope\* revealed numerous interface pieces thin enough for transmission in the samples prepared in HCl solution diluted by methanol or in concentrated HCl solution and a few thin interface layers in the sample etched by KOH.

Both the composite wire and plate were fractured in situ in the Scanning Auger Microscope (SAM)\*\* under  $10^{-3}$   $\mu$ Pa vacuum

\*A JEOL 150 KeV TEM was used in the transmission diffraction studies.

\*\*The SAM instrument applied in these studies was the Physical Electronics model 590 system.

in order to unambiguously analyze the material in the fractured interface region between fiber and matrix. In addition, some of the samples were sputtered using 5kV argon ions and examined to identify the chemical species present. An electron beam spot size of approximately  $1\mu$  or less was used to give good spatial resolution and high signal to noise ratio.

#### Results and Discussion

The most often observed phase was a  $TiB_2$  hexagonal structure which was found in all the pretreated materials studied here. Some typical electron diffraction patterns of  $TiB_2$  prepared in HCl plus methanol for various composite materials are shown in Figure 2. The observation of the spotty nature of the rings in the  $TiB_2$  diffraction pattern from the T114A composite indicated that the grain size of  $TiB_2$  in the T114A composite was larger than the grain size of  $TiB_2$  in the other composites studied here. This grain size difference was consistently observed in many fibers and also in samples prepared by the other selective etchants: concentrated HCl and KOH. One basic difference between T114A and the rest of the composite materials is that the fiber in T114A has the graphite basal plane parallel to the fiber surface but the other composites have the pitch type fiber with basal plane perpendicular to the surface. This difference in

crystallographic orientation in the substrate may lead to a preferential growth of large grains for a  $\text{TiB}_2$  reaction product in T114A. The grain size effect may play a role in the transverse properties of the composites.

In recent years it has been demonstrated that a high degree of preferred orientation of "fibrils" are formed in the graphite fiber of high tensile modulus and strength<sup>[4]</sup>. The "fibril" is a structural unit which is composed of

"microfibrils" and pore structure<sup>[5,6]</sup>. Its dimensions have been estimated to be from  $250\text{\AA}$  to as high as  $1000\text{\AA}$ <sup>[7,8]</sup> in the transverse direction. The fibrils have indefinite length and may form a continuous or branched network. The "microfibril" is a stacking of graphite layers and the dimensions can be characterized by the stacking height (or the microfibril thickness) and the microfibril width and length.

A close investigation into the morphology of  $\text{TiB}_2$  layer in electron micrographs for various composites showed some striated or ripple characteristics of this interface layer in pitch fiber reinforced materials (see Figure 3). These ripples are probably due to the "fibril" structure. The chemical vapor deposited  $\text{TiB}_2$  covers the fiber surface as a surface replica. A rough estimation of the dimension across these strips gives values ranging from  $200\text{\AA}$  to  $600\text{\AA}$  which are in the range of fibril transverse dimension.

The micrographs of  $\text{TiB}_2$  layer formed at the interface for low modulus PAN II composites are also shown in Figure 4. The comparison between pitch fiber and low modulus PAN II composites can be seen in Figure 3 and Figure 4, respectively, where the  $\text{TiB}_2$  phase with crenulations or ripples for VSB 32 pitch type composites and without for PAN II type composites are presented. The diffraction pattern of Figure 3 (c,d) is shown in Figure 2 (b) and that of Figure 4 is shown in Figure 2(c).

An aluminum oxide ( $\gamma\text{-Al}_2\text{O}_3$ ) phase was often observed along the fiber/matrix interface. The origin of the oxide has not been clearly established, but it is most likely the reaction product of oxygen which was contained in the fibers and then segregated to the interface during the aluminum-infiltration processing step. The exact role of this oxide layer is not known at present, but the recent SAM studies<sup>[9]</sup> indicate that it seems to promote matrix adhesion to the graphite which might be responsible for an increased transverse strength in graphite/aluminum composites. The present TEM examination of these oxide layers on the fiber surfaces indicated that the  $\gamma\text{-Al}_2\text{O}_3$  phase has a relatively larger grain size on the average than that of  $\text{TiB}_2$ . The electron diffraction patterns of  $\gamma\text{-Al}_2\text{O}_3$  (Fig. 5) were observed for the composites with an interface coating and the single fiber wire which had no coating on the interface.



It is also interesting to point out that titanium carbide, TiC, was observed in G3842 and G3636 composites. In both materials, the rings of diffraction pattern are continuous, however the diffraction ring is broadened to some extent in G3636 composite. This is believed to be due to the effect of very fine grain size. The diffraction pattern and micrograph for the TiC phase can be seen in Figure 7.

The  $\text{Al}_4\text{C}_3$  phase which was determined<sup>[10]</sup> to be present at the interface in other research (Aerospace Corp.) could not be identified by the technique used here, because  $\text{Al}_4\text{C}_3$  is decomposed in water and highly soluble in both acid and alkali solution. Recently  $\text{Al}_4\text{C}_3$  as well as oxides other than  $\text{Al}_2\text{O}_3$  have been observed using an electrochemical thinning technique. Further studies using this approach are now in progress.

The interface reaction zone in the composites studied in the TEM was also investigated by SAM combined with in situ fracture to help identify the interface chemistry. The fracture paths were through the oxide layer or close to either the fiber side or matrix side of the interfaces. The Auger chemical analysis versus the depth into the fracture surface was obtained using inert argon ion sputtering. Using sensitivity factors<sup>[11]</sup> estimation of the atomic concentration ratio of titanium to boron, Ti/B at selected points after

sputtering was consistently about 0.51-0.57 in the G3636 and G3842 materials (see Figures 8 and 9). A standard  $\text{TiB}_2$  Auger spectra after sputtering of  $\text{TiB}_2$  powder is shown in Fig. 10. The Ti/B ratio is  $\sim 0.55$ . A lack of chemical shift in peak location and consistent peak to peak height analysis together with the assumptions that the escape depth correction, back scattering factor and surrounding chemical effect are negligible, support the TEM results that  $\text{TiB}_2$  phase was present in the interface layer. Further studies are being conducted in the TEM and SAM to clarify and extend the results reported in this paper.

### Conclusions

Results of this work can be summarized as follows:

1.  $\text{TiB}_2$  phase is generally present for the aluminum/graphite composites processed by standard pretreatment coating technology.
2. Larger  $\text{TiB}_2$  phase grain size was observed in PAN II fibers with the graphite basal plane perpendicular to the fiber surface. This could relate to higher transverse strength in composites with this fiber.
3.  $\gamma\text{-Al}_2\text{O}_3$  phase was found in most composites and is relatively larger in grain size than the  $\text{TiB}_2$  phase.

4. The mixture of  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{TiB}_2$  was observed in some areas of interface for the composite with pitch fibers.
5. AES identified the existence of the approximately stoichiometric  $\text{TiB}_2$  atomic concentration ratio, for many of the composites studied.

#### Acknowledgement

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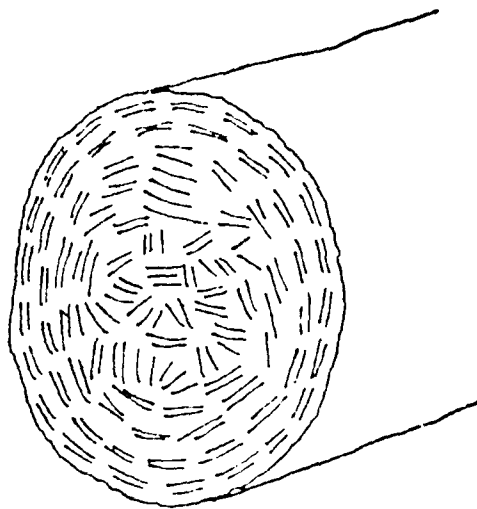
Table 1

Composite Materials	Graphite Fiber Type	*Transverse Strength MPa	**Phase(s) Observed in TEM
T114A	PAN II (Celion 6000)	76	TiB <sub>2</sub> , γ-Al <sub>2</sub> O <sub>3</sub>
G3842 (made from T133)	Pitch (VSB-32)	31	TiB <sub>2</sub> , γ-Al <sub>2</sub> O <sub>3</sub> , TiC
G3636 (made from T105A)	Pitch (VSB-32)	10	TiB <sub>2</sub> , γ-Al <sub>2</sub> O <sub>3</sub> , TiC
T109B	Pitch (VSB-32)	not available	TiB <sub>2</sub>
HM pitch/ 6061	HM 3000	14-80 depends on consolidation process	TiB <sub>2</sub>
Single Fiber Wire	PAN II (Celion 12000)	not measured	γ-Al <sub>2</sub> O <sub>3</sub>

\*Transverse Strength was tested in plate forms by Aerospace Corporation.

\*\*Camera constant used here for d-space identification was about 1.37 Angstrom-cm.

PAN



PITCH

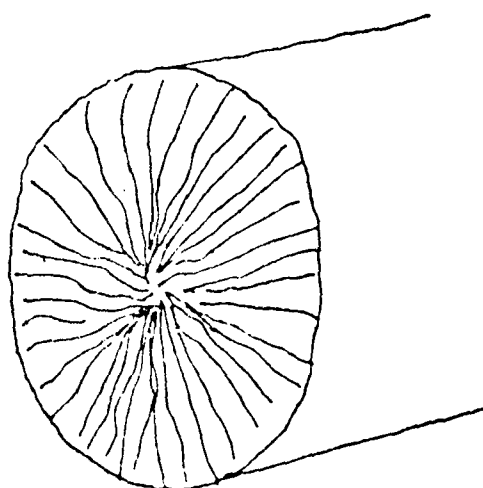


Fig. 1. Schematic diagram of oriented structure in PAN and Pitch type fibers.

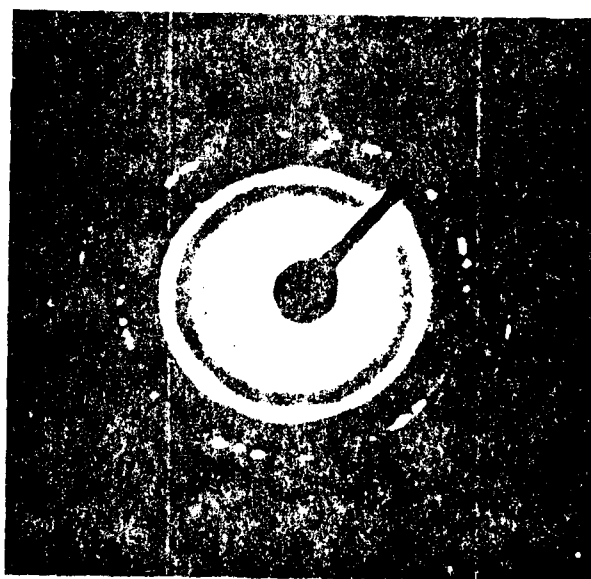
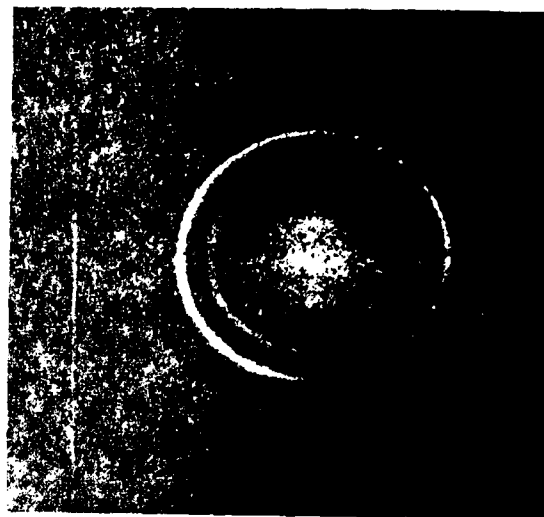
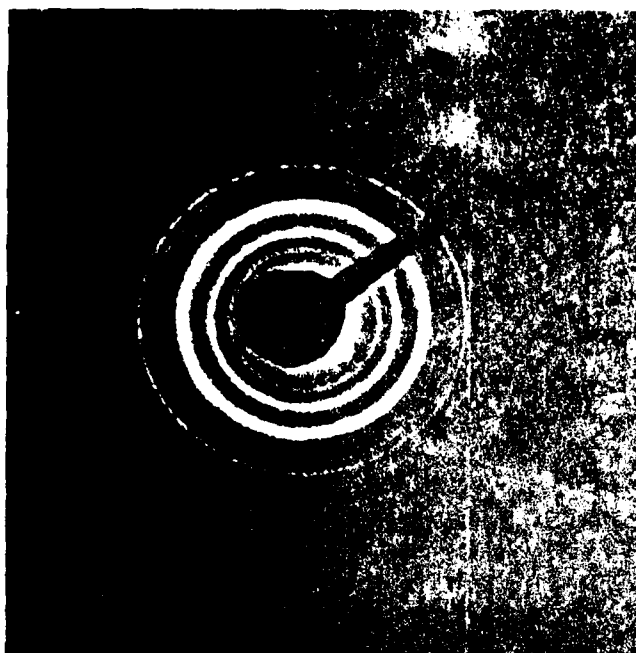
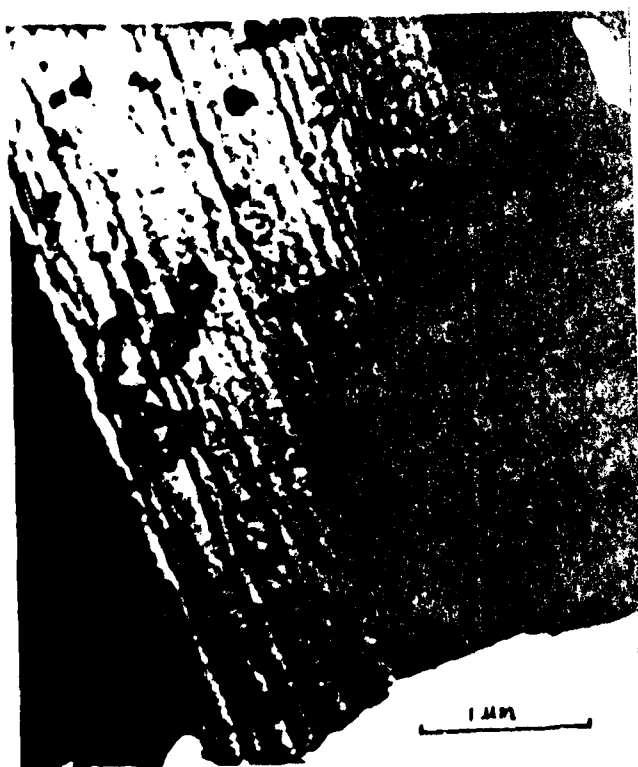
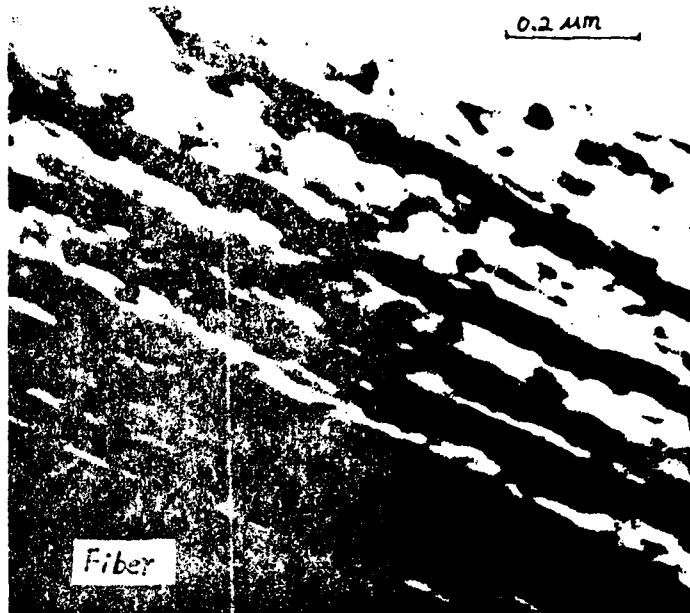


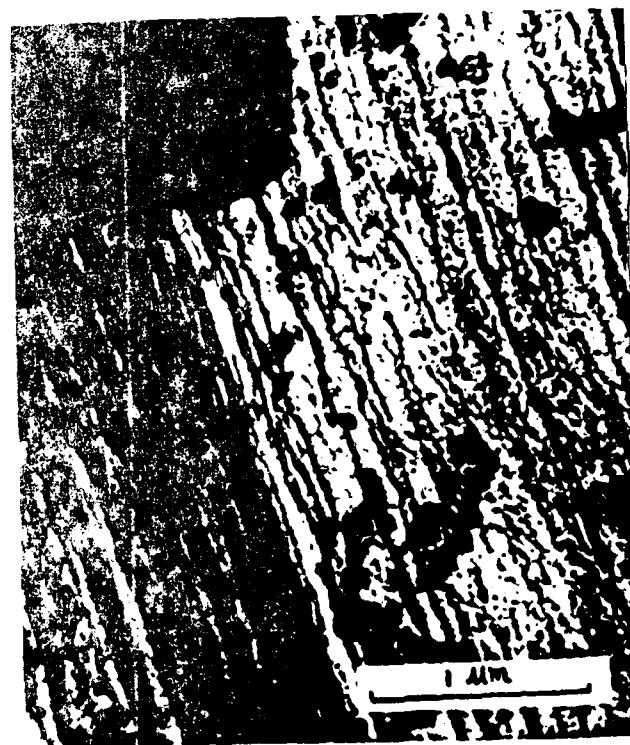
Fig. 2. Electron diffraction patterns for (a) 100 and (b) 110 GPa. (a) G30 for 100 GPa, (b) G30 for 110 GPa, (c) 1104 for 100 GPa, (d) 1104 for 110 GPa, (e) 1104 for 120 GPa, (f) 1104 for 130 GPa, (g) 1104 for 140 GPa, (h) 1104 for 150 GPa, (i) 1104 for 160 GPa, (j) 1104 for 170 GPa, (k) 1104 for 180 GPa, (l) 1104 for 190 GPa, (m) 1104 for 200 GPa, (n) 1104 for 210 GPa, (o) 1104 for 220 GPa, (p) 1104 for 230 GPa, (q) 1104 for 240 GPa, (r) 1104 for 250 GPa, (s) 1104 for 260 GPa, (t) 1104 for 270 GPa, (u) 1104 for 280 GPa, (v) 1104 for 290 GPa, (w) 1104 for 300 GPa, (x) 1104 for 310 GPa, (y) 1104 for 320 GPa, (z) 1104 for 330 GPa, (aa) 1104 for 340 GPa, (ab) 1104 for 350 GPa, (ac) 1104 for 360 GPa, (ad) 1104 for 370 GPa, (ae) 1104 for 380 GPa, (af) 1104 for 390 GPa, (ag) 1104 for 400 GPa, (ah) 1104 for 410 GPa, (ai) 1104 for 420 GPa, (aj) 1104 for 430 GPa, (ak) 1104 for 440 GPa, (al) 1104 for 450 GPa, (am) 1104 for 460 GPa, (an) 1104 for 470 GPa, (ao) 1104 for 480 GPa, (ap) 1104 for 490 GPa, (aq) 1104 for 500 GPa, (ar) 1104 for 510 GPa, (as) 1104 for 520 GPa, (at) 1104 for 530 GPa, (au) 1104 for 540 GPa, (av) 1104 for 550 GPa, (aw) 1104 for 560 GPa, (ax) 1104 for 570 GPa, (ay) 1104 for 580 GPa, (az) 1104 for 590 GPa, (ba) 1104 for 600 GPa, (bb) 1104 for 610 GPa, (bc) 1104 for 620 GPa, (bd) 1104 for 630 GPa, (be) 1104 for 640 GPa, (bf) 1104 for 650 GPa, (bg) 1104 for 660 GPa, (bh) 1104 for 670 GPa, (bi) 1104 for 680 GPa, (bj) 1104 for 690 GPa, (bk) 1104 for 700 GPa, (bl) 1104 for 710 GPa, (bm) 1104 for 720 GPa, (bn) 1104 for 730 GPa, (bo) 1104 for 740 GPa, (bp) 1104 for 750 GPa, (bq) 1104 for 760 GPa, (br) 1104 for 770 GPa, (bs) 1104 for 780 GPa, (bt) 1104 for 790 GPa, (bu) 1104 for 800 GPa, (bv) 1104 for 810 GPa, (bw) 1104 for 820 GPa, (bx) 1104 for 830 GPa, (by) 1104 for 840 GPa, (bz) 1104 for 850 GPa, (ca) 1104 for 860 GPa, (cb) 1104 for 870 GPa, (cc) 1104 for 880 GPa, (cd) 1104 for 890 GPa, (ce) 1104 for 900 GPa, (cf) 1104 for 910 GPa, (cg) 1104 for 920 GPa, (ch) 1104 for 930 GPa, (ci) 1104 for 940 GPa, (cj) 1104 for 950 GPa, 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(a)



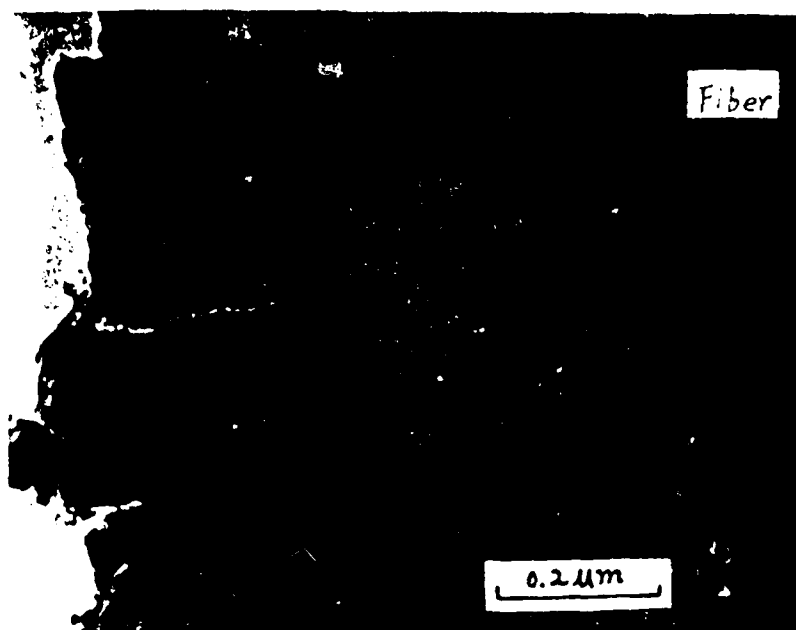
(c)



(d)

Fig. 3 Electron micrographs showing the internal structure of the layers in various pitch fibers. The scale bar is in microns. (a) 11000, (b) 10000, (c) 63812, and (d) 63812 etched by nitric acid.





(b)

Fig. 4. Electron micrographs of larger grain size TiB<sub>2</sub> phase in Ti-4V: (a) sample etched by KOH, (b) sample etched by HCl and methanol.



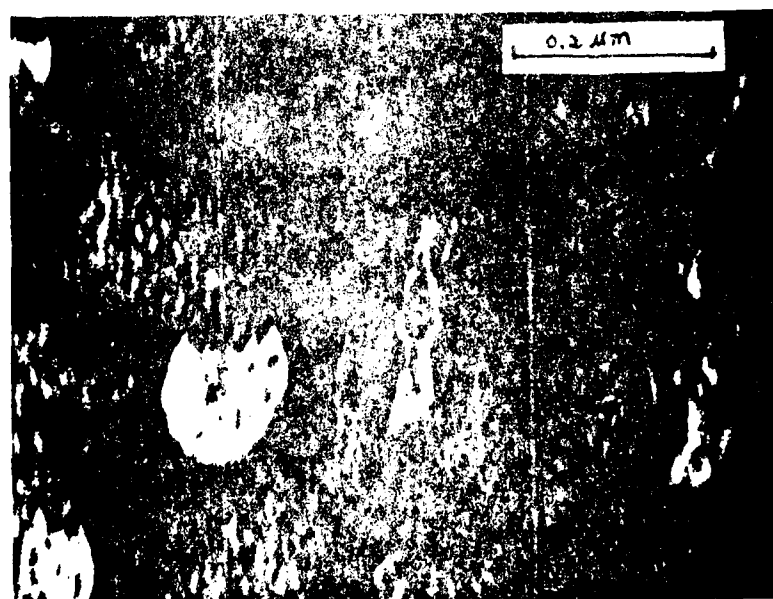
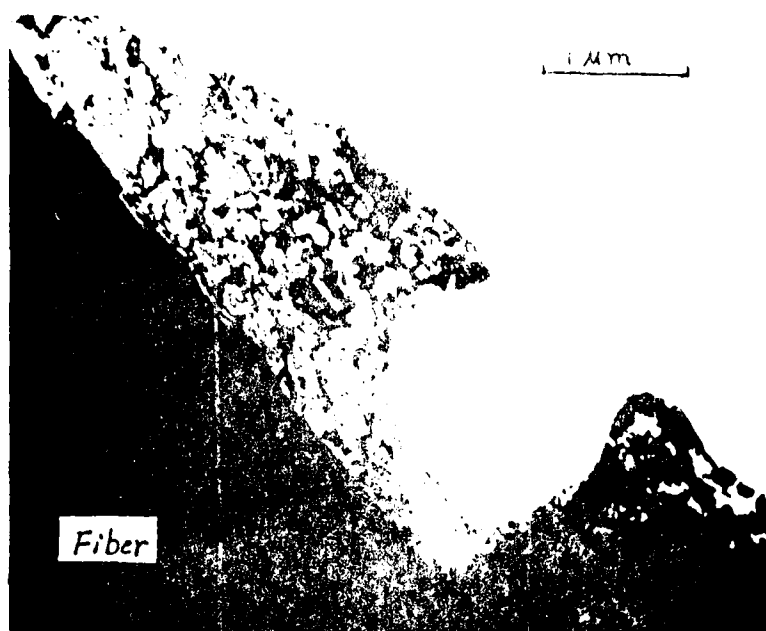


Fig. 6. Micrographs of whole piece of H14A etched by HCl and methanol. (a) Low magnification of whole piece, the dark part is fiber. (b) High magnification of center area of the whole piece. Note: Some larger grain like structure in the neck part of the whole piece is also observed.

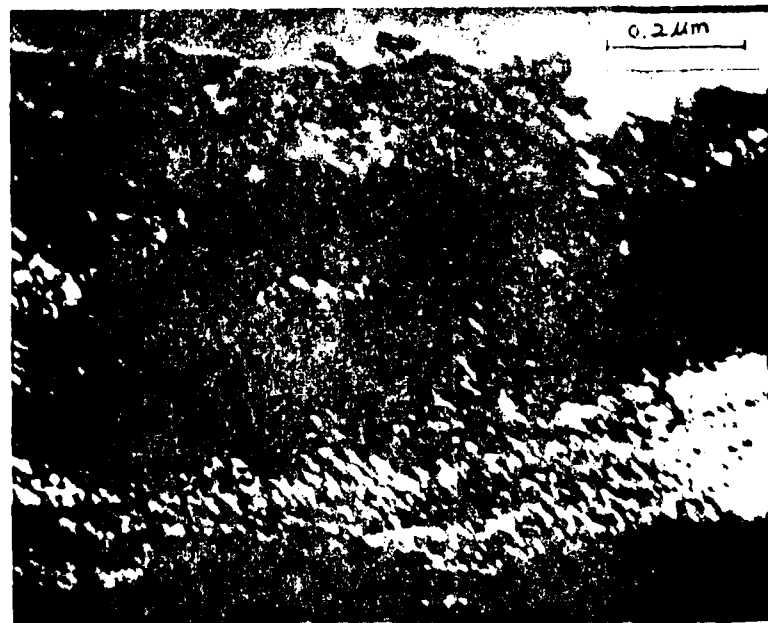
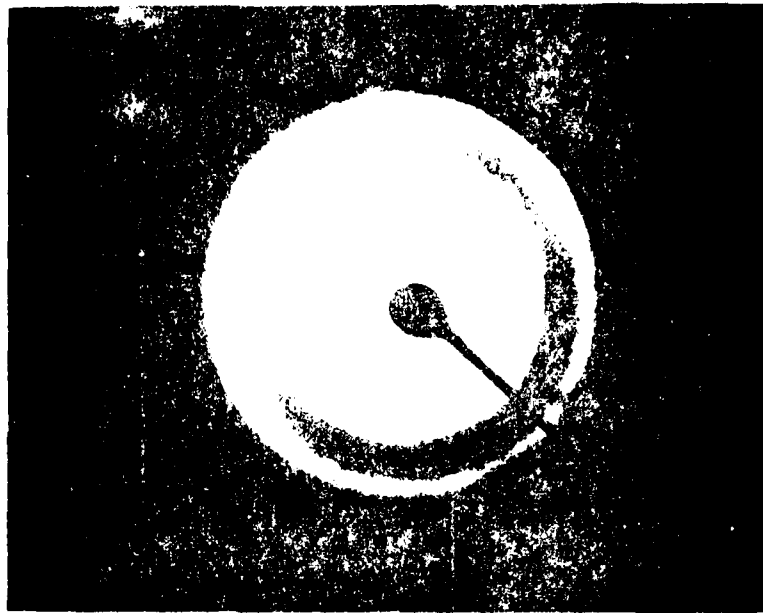


Fig. 7. The microstructure of the surface of the film (a) a diffused electron micrograph; (b) a transmission electron micrograph of (a).

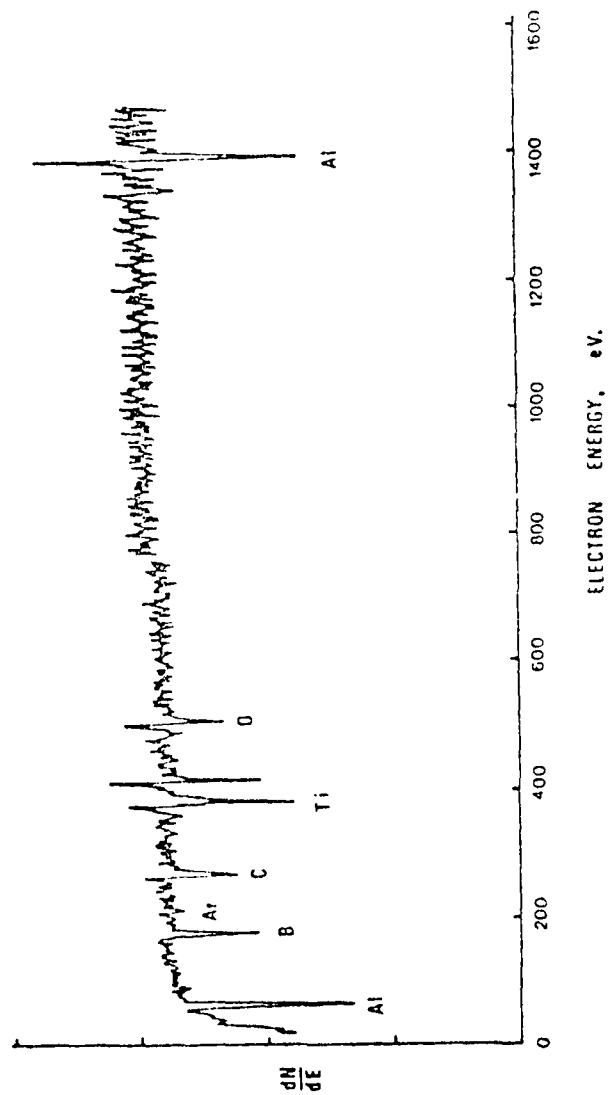


Fig. 8. AES analysis of the fractured interface after 25 minute sputtering in T105A (plate G3636 was used).

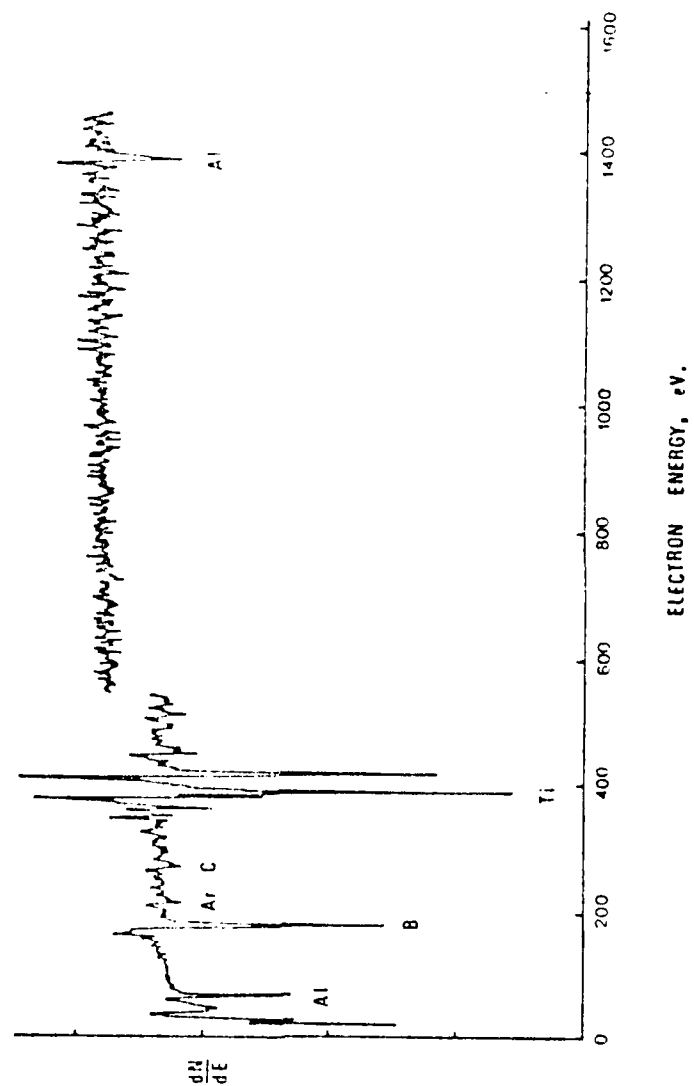


Fig. 9. AES analysis of the fractured interface after 5 minute sputtering in G3842.

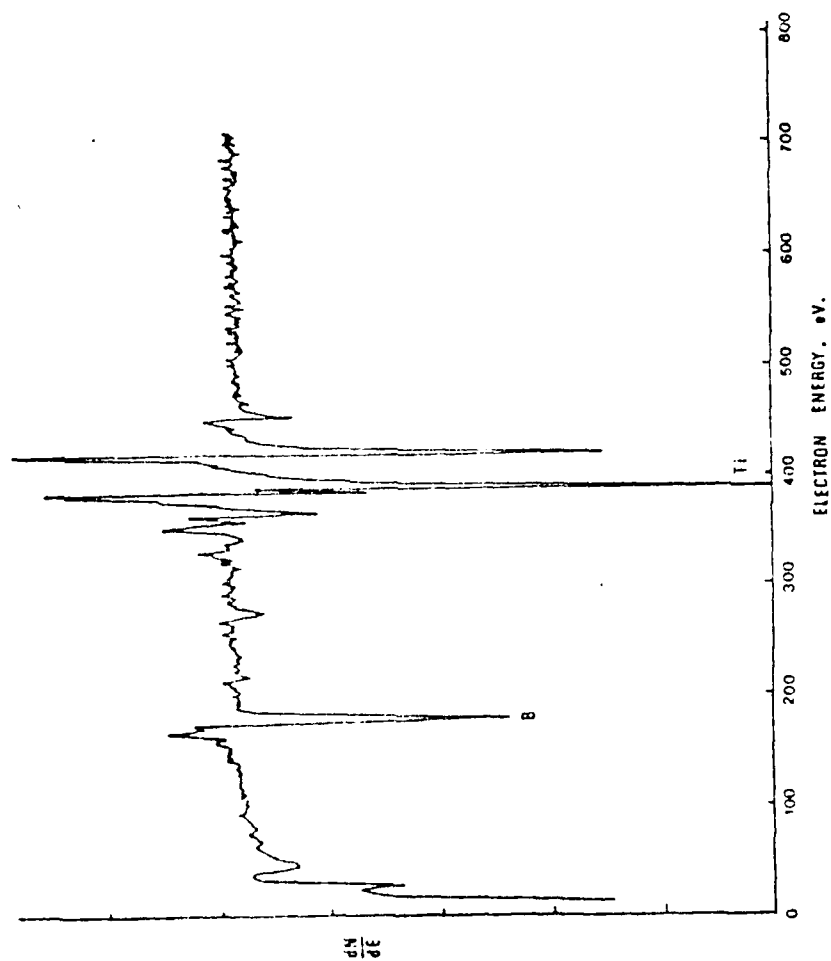


Fig. 10. Standard  $\text{TiB}_2$  SAN spectra after sputtering.